

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B29C 41/00, 41/14, 41/22	A1	(11) International Publication Number: WO 96/25279 (43) International Publication Date: 22 August 1996 (22.08.96)
(21) International Application Number: PCT/US96/01816 (22) International Filing Date: 9 February 1996 (09.02.96) (30) Priority Data: 08/388,309 14 February 1995 (14.02.95) US (71) Applicant: BAXTER INTERNATIONAL INC. [US/US]; One Baxter Parkway, Deerfield, IL 60015 (US). (72) Inventor: PLAMTHOTTAM, Sebastian, S.; 1496 Moonridge Court, Upland, CA 91784 (US). (74) Agents: STENZEL, Robert, A. et al.; One Baxter Parkway, Deerfield, IL 60015 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KG, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: A MULTIPLE DIP PROCESS FOR MAKING A POWDER-FREE ARTICLE		
(57) Abstract The present invention involves a process of making a powder-free rubber article using a multiple dip process. The process comprises the steps of: a) dipping a former of the desired shape of the article into a composition consisting essentially of an aqueous acrylic ester latex and water soluble salts capable of coagulating a rubber latex; b) dipping the former in step (a) into a rubber latex to produce a second layer; c) leaching the second layer in water; d) curing the first and second layers; and e) stripping the resultant article from the former. The acrylic ester latex is a water insoluble polymer emulsion in water. The polymer is composed predominantly of acrylic ester groups which make up at least 50 % by weight of the polymer.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

A MULTIPLE DIP PROCESS FOR MAKING A POWDER-FREE ARTICLE

FIELD OF THE INVENTION

The present invention relates to a process of making a powder-free rubber article. More specifically, the present invention relates to a process of making powder-free articles, particularly gloves, using a multiple dip process.

BACKGROUND OF THE INVENTION

Traditionally, rubber articles such as gloves were manufactured by dipping a former or mold into a rubber latex. These processes often included the use of a powdered lubricant, such as talc, cornstarch, or clay. Typically, the powder was incorporated into either a coagulant or into a release slurry. A coagulant is a compound that coagulates a layer-forming emulsion or dispersion to form a thicker layer than it would normally do otherwise. A release slurry is a slurry containing powder which is applied to the article prior to removal from the former. The use of powder in the coagulant or release slurry served two important purposes. First, powder made it easier to strip the resulting article from the former. With respect to gloves, removal from the mold is often difficult because cured latex gloves tend to be tacky and adhere to the mold. However, the use of powder reduced the tackiness or stickiness of the gloves and improved

stripping. Second, powder facilitated donning in certain articles such as gloves.

While the use of powder in the manufacture of rubber articles solved many problems, it created many new ones as well. The main problem was that the completed rubber article contained a great deal of residual powder. It is well known in the art that this residual powder can create numerous problems, particularly with respect to surgical gloves where there is a risk that the powder may escape from the glove and contaminate the surgical field. See Alexander's Care of the Patient in Surgery 9th Edition. Another problem commonly associated with the use of powder is that the process requires cleaning up the powder residue on the former after formation of each and every article, a tedious and time consuming operation. Because of these problems, numerous attempts have been made to eliminate the use of powder in the construction of articles. For a detailed description of making rubber articles see: Natural Rubber Dipping Technologies, Symposium on Latex as a Barrier Material, April 6 and 7, 1989, University of Maryland; Russell D. Culp and Bradley L. Pugh. This publication is incorporated herein by reference.

Several processes are known in the art for making powder-free articles.

PRIOR ART

In one process to make the article powder-free, the article is halogenated, normally with chlorine, in a batch process. For example, U.S. Patents 3,411,982
5 and 3,740,262 disclose that the surface of a rubber glove can be halogenated to make it slippery. U.S. Patent 4,304,008 discloses that halogenation facilitates donning in rubber articles in lieu of powdered lubricants. U.S. Patent 3,740,262 discloses
10 halogenating a glove to provide a powder-free rejecting outer surface and a powder-accepting inner surface.

Halogenation produces articles having a powder-free clean surface. In fact, chlorination is widely used to make clean-room gloves, powder-free surgical
15 gloves and powder-free examination gloves. Although articles produced using chlorination are powder-free and exhibit good dry donning characteristics, they are economically more expensive to produce due to the number of chlorination steps, turning steps, and drying
20 processes involved in the manufacture.

While halogenation can be used to facilitate donning, halogenated articles possess many disadvantages. Halogenated articles tend to discolor and age poorly both in storage and in use. In fact,
25 discoloration can begin almost immediately, and within a month, the halogenated surface may become hard and brittle and brown in color. Additionally, chlorine is

considered to be a toxic chemical and disposal of materials containing this element presents numerous environmental issues.

The disadvantages of chlorination are recognized
5 in U.S. Patent 5,284,607. This patent discloses a process for making a multi-layered, powder-free medical glove. The glove is made with an acid-soluble powder, and once fully formed, stripped from the former and reversed so that the first layer is on the outside.
10 The glove is then treated with an acid, such as nitric acid, to remove the acid-soluble powder. After the acid treatment, the glove is rinsed with water and treated with bleach to chlorinate the inner and outer glove surface. The bleach does not cause the glove to
15 have the excessively slippery outer surface that typically results when chlorination is used.

U.S. Patent 4,310,928 discloses a talc free surgeon's glove. The glove is made by dipping a former into a coagulant solution containing a lipo compound
20 and a surfactant and then into latex to form a glove.

U.S. Patent 4,499,154 discloses another method of making a powder-free article. This patent details a process for making a rubber article by dipping a former into compounded latex, leaching the article, priming
25 the article with an acid, neutralizing the article with water or an aqueous alkali, applying a hydrophilic coating, heating the article to fix the coating, curing

the rubber, stripping the article from the former and applying a solution of surfactant materials and silicone. While this process produces a powder-free article, the number of steps involved makes the process unduly expensive and the low molecular weight components (surfactants and silicone) could cause contamination.

U.S. Patent 5,138,719 discloses a method of making powder-free gloves, finger stalls and other protective articles constructed from latex and microcapsules. The microcapsules are dispersed and arranged in the latex to form a concentration gradient, with the concentration of the microcapsules increasing progressively from the outer surface to the inner surface of the article. The high concentration of the microcapsules at the inner surface provides good sliding properties and facilitates donning without the need for powder. In addition, the microcapsules may contain a pharmaceutically active substance such as nonoxynol, moroxydine hydrochloride, vidarabine to provide viricidal activity against diseases such as AIDS or herpes. See U.S. Patent 5,024,852.

EP 0574160A1 discloses a method for making a powder-free, wet and dry donnable, multi-layered article having a first layer formed from natural rubber, a second layer formed from natural rubber, polyurethane, poly(acrylamide/acrylic acid) and

polyethylene oxide, and a third layer of an acrylic copolymer and fluorocarbon telomer resin.

U.S. Patent 3,411,982 discloses a method for making an elastomeric article having a slip coating.

5 In one embodiment, the method involves first dipping a former into talc or some other releasing agent which leaves a powder residue. The former is next dipped into a slip dip compound made of a rubber-resin compound that contains a coagulant and a stabilizing
10 surfactant. The former is removed from the slip dip compound and allowed to dry. Once dried, the former is dipped into latex to form the desired article. After dipping in the latex, the former is withdrawn and leached in water. After leaching, the article is dried
15 or cured and then stripped from the former. Articles produced according to the above process, while multi-layered, are not powder-free.

A different process for making rubber gloves alleged to have good donning properties is disclosed in
20 Kavalir et al., U.S. Patents 3,286,011 and 3,411,982. The disclosures of these patents are the same. These patents a coating composition comprising a mixed latex which is approximately 1:1 on a weight basis of a rubber latex and certain resinous polymer latices. One
25 group of these polymer latices are certain acrylic ester latices. The compositions of the patent are suggested for use as being former coatings and as

coatings for the inner surfaces of rubber gloves to impart improved donning characteristics. The acrylic ester latices used by the patentees in their process are mixtures of acrylic ester latices. These acrylic latices and their method of manufacture are described in detail as well in U.S. Patent 2,795,564 the disclosure of which is incorporated herein by reference.

One of the teachings of the Kavalir et al. patents is that high concentrations of coagulating salts may be incorporated into the coating compositions of the invention. The use of a water soluble non-ionic surfactants incorporated into the compositions of the patent allows for the introduction of large quantities of coagulating salts such as calcium nitrate without resulting in the destabilization of the compositions. The patentees stress that the resinous polymer latices alone without the rubber latex are inoperative. Other disadvantages become apparent from the study of these patents. Powders such as talc, are needed to provide former release. Also, the compositions of the patentees are high solids viscous compositions making them difficult to apply either to formers or articles formed thereon. Thus, while providing and interesting approach to improved glove making this patent still does not solve the problem of eliminating powders as lubricants.

OBJECTS OF THE INVENTION

An object for the present invention is to provide a simplified process of making powder-free articles, particularly gloves, using multiple dip coating technologies with carefully engineered functional inner and outer layers. Articles made in this manner can be produced in a continuous fashion, with substantial economic savings, and added features and benefits. In addition, environmentally friendly materials and processes can be used if water borne systems are selected for use in conjunction with this process. Importantly the invention provides for good release of the articles from the formers upon which they are produced. In the case of gloves produced by the process of the invention exhibit excellent dry and some good wet donning characteristics.

SUMMARY OF THE INVENTION

The present invention provides a process of making a powder-free rubber article using a multiple dip process. In particular, this process can be used to make powder-free articles such as surgical and examination gloves, catheters and condoms. The method disclosed in this application may be used in other medical applications such as in the construction of surgical operative fields, finger stalls, aprons, bibs, and caps.

The invention comprises a multiple dip process for making powder-free rubber articles, particularly gloves. It comprises the steps of:

- a) dipping a former of the desired shape of the article into a composition consisting essentially of an aqueous acrylic ester latex and water soluble salts capable of coagulating a rubber latex. The acrylic ester latex is a water insoluble polymer emulsion in water. The polymer is composed predominantly of acrylic ester groups which make up at least 50% by weight of the polymer. The dip into the acrylic ester latex causes a first layer lubricating coating to be formed on the former.
- b) dipping the former treated in step (a) into a rubber latex to produce a second layer;
- c) leaching the second layer in water;
- d) curing the first and second layers; and
- e) stripping the resultant article from the former.

The process thus described may be modified by the additional step of applying the composition described above which does not contain the water soluble salts to the second layer prior to curing. It may be further modified by the additional step of applying the composition to the article prior to stripping, but after curing, and then drying.

The aqueous acrylic ester latex preferably is an

acrylic acid or methacrylic acid ester latex which is synthesized from acrylate esters containing from 4 to 22 carbon atoms. In another desirable embodiment, the aqueous acrylic ester latex is a copolymer which
5 contains from 2-3 monomers. It may be a mixture of acrylic esters. In another preferred embodiment of the invention the acrylic esters contain from 0.1 to 20 weight percent of either acrylic or methacrylic acid.

Additionally, improved mold release
10 and donning characteristics are achieved when the acrylic ester latices described above are combined with from 0.001 to 3% by weight of a silicone resin.

The invention is also directed to formers of the type used to make gloves and similar articles which
15 contain an easy release coating of the compositions described above. It also relates to gloves and similar articles having on their inner surfaces a coating of the compositions of the invention which do not contain the water soluble rubber latex coagulating salts which
20 coatings provide good donning properties.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a multiple dip process for producing a powder-free rubber article. As used in the specification and appended claims, "powder-free"
25 means that the article has been manufactured to eliminate most, if not all, of the powder on the

surface of the article.

To produce a powder-free article, a cleaned former or mold in the shape of the desired article is first dipped or immersed into a coagulation inducing, powder-free composition to form a coagulation inducing film.

5 The coagulation inducing, powder-free composition functions as a coating thereby eliminating the need for a powdered coagulant. The coagulation inducing, powder-free composition is an acrylic latex that

10 contains coagulant salts. Methods for making polymer dispersions or emulsions are well known in the art. See Blackley, High Polymer Latices Vol. 1 and 2, MaClaren & Sons, Ltd., 1966, pgs. 266-270. Acrylated ester latex preparations are described in detail in

15 U.S. Patent 2,795,564. The acrylate ester latices contemplated for use in the coagulation inducing, powder-free composition are those polymers which will provide a good coating, eliminate the need for powder, will not block and will not stick to itself or other

20 substrates. Additionally, it is also important that these latices have sufficient electrolyte stability to accommodate the coagulant salts used in the formulation. As used in this specification, "electrolyte stability" means that the polymer

25 suspension does not destabilize when the coagulant salt is added. The electrolyte stability can be determined by adding coagulant salts to the polymer suspension and

observing whether the polymer destabilizes. If destabilization occurs, chunks of the polymer are observed floating or settling in the dispersion or emulsion. See Blackley, p. 27. The stability of the
5 acrylate ester latex containing the coagulant salts can be improved by combining therewith stabilizing amounts of surfactants, particularly non-ionic surfactants as described in the Kavalir et al. patents.

An important modification that may be used to
10 improve the anchorage of the acrylate ester polymers is to incorporate into these polymers between about 0.01-10% by weight of an allyl acrylate. Preferably the amount of the allyl acrylate is between 1-5% by weight.

15 The Acrylic Ester Latices

The latices may be prepared by homo or copolymerizing one or more acrylic esters. The polymerizations are performed in the presence of free radical catalysts which are described and illustrated
20 in the references previously cited. The acrylic esters that may be used may be either acrylic acid esters that produce soft or hard polymers.

As polymerizable, neutral monomeric monovinylidene esters which form soft, solid polymers in the presence
25 of peroxidic catalysts, there may be used any primary and secondary alkyl acrylate, even with alkyl substituents up to eighteen or more carbon atoms,

primary or secondary alkyl substituents of five or
eighteen or more carbon atoms, or other monovinylidene
compounds as defined above which are polymerizable
below 80°C. with free radical catalysts to form soft
5 solid polymers. Ionically polymerizable compounds are
not within the scope of this class of compounds. The
preferred monovinylidene compounds are the stated
acrylates and methacrylates and of these the most
practical esters are those with alkyl groups of not
10 over 12 carbon atoms.

The preferred monomers which by themselves yield
soft polymers may be summarized by the formula



where R is hydrogen or the methyl group and R^x
represents, when R is methyl, a primary or secondary
alkyl group of 5 to 18 carbon atoms, or, when R is
hydrogen, an alkyl group of not over 18 carbon atoms,
20 or better, of two to 12 carbon atoms.

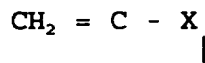
Typical compounds coming within the above
definition are methyl acrylate, ethyl acrylate, propyl
acrylate, isopropyl acrylate, butyl acrylate, isobutyl
acrylate, sec.-butyl acrylate, amyl acrylate, isoamyl
25 acrylate, hexyl acrylate, 2-ethylhexyl acrylate, octyl
acrylate, 3,5,5-trimethylhexyl acrylate, decyl
acrylate, dodecyl acrylate, cetyl acrylate, octadecyl
acrylate, octadecenyl acrylate, n-amyl methacrylate,

sec-amyl methacrylate, hexyl methacrylate, 2-ethyl
methacrylate, octyl methacrylate, 3,5,5-trimethylhexyl
methacrylate, decyl methacrylate, dodecyl methacrylate,
octadecyl methacrylate, butoxyethyl acrylate or
5 methacrylate or other alkoxyethyl acrylate or
methacrylate, etc.

As polymerizable monovinylidene monomers which by
themselves form hard polymers, there may be used alkyl
methacrylates having alkyl groups of not over four
10 carbon atoms, also tert.-amyl methacrylate, tert.-butyl
or tert.-amyl acrylate, cyclohexyl acrylate or
methacrylate, acrylonitrile, or methacrylonitrile.

The above monomers yield polymers under the
influence of free radical catalysts, particularly
15 peroxidic catalysts, which polymers are generally
regarded as hard. These polymers when free of any
appreciable content of monomer, have Tg values above
about 20°C. Hard polymers have also been defined as
those having softening points above 55°C or brittle
20 points above about 5°C. These are all different
appraisals of the force required to produce a given
deformation in a body in a given time and to evaluate
the aggregation of various properties encompassed
within the term of hardness.

25 Preferred monomers which by themselves form hard
polymers may be summarized by the formula



R

wherein R is a hydrogen of the methyl group and wherein X represents one of the groups -- CN, and ester-forming groups -- COOR', wherein R' is cyclohexyl or, when R is hydrogen, a tert.alkyl group of four to five carbon atoms, or, when R is methyl an alkyl group of one to four carbon atoms. Some typical examples of these have already been named. Other specific compounds are methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate, sec.-butyl methacrylate, and tert.-butyl methacrylate.

When the hard acrylic esters are used in the practice of the invention they tend to form brittle films. To render the films of these polymers more flexible it is beneficial that they be polymerized with other monomers to render them less brittle when subject to forces of stretching, crushing and the like. These hard acrylic esters may be improved in their properties by copolymerizing them with soft acrylate esters or other monomers. Even in the case of the soft acrylate ester latex polymers benefits may be derived by incorporating into the structure of these polymers other monomers that improve their film forming and lubricating effectiveness. One of the most beneficial group of monomers that may be copolymerized with acrylate esters are the acrylic acids.

The Acrylic Acid Monomers

As indicated these monomers are incorporated into the acrylic ester latices used in the practice of the invention in amounts ranging from between 0.1 - 20 % by weight. The amount to be used will depend on the properties of the acrylic ester latex with which they are polymerized. Optimization can be determined by the use of routine experimentation.

The preferred acids are methacrylic and then acrylic. In place of the free acids there may be used water-soluble salts thereof, including the ammonium salts and the alkali metal salts such as lithium or potassium carboxylates. The salts may be preformed or they may be formed in the dispersion system. The necessary and important consideration is that carboxylate groups be supplied to enter into the interpolmer. The best way to ensure that carboxylate groups do in fact enter into the copolymer chain is to use an above acid.

20

Other Monomers

While acrylic acid or methacrylic acid and their salts may be used to modify the acrylic ester latices to improve their usefulness other modifications of the acrylic ester latices may be made. It is well known that acrylate ester latex homo and copolymers may be polymerized with a variety of monomers to change the

physical properties of these polymers. When such additional monomers are copolymerized with the acrylic esters they should be used in amounts that do not change the basic characteristic of the acrylate esters.

5 Highly polar monomers such as acrylamide must be used judiciously to avoid converting the acrylic ester latices from their normal state of water insolubility to water solubility or dispersability. Usually when polar vinyl monomers are used as modifiers for the

10 acrylate ester latices they should rarely exceed 20 % by weight. Preferably they should not exceed 10% by weight.

Other monomers may be polymerized with the acrylic esters to provide different properties to the finished

15 latex. For instance plasticizers may be built into the acrylic ester polymers by using up to about 5% of a vinyl glycol ester. In a similar fashion improved lubricity may be achieved by incorporating into the acrylic ester polymers from 0.1 to about 10% by weight

20 of copolymerizable surfactants such as polar fatty compounds. Alternatively, surfactant type molecules can be introduced by the ethoxylation of the acrylic esters when they contain active hydrogen atoms capable of reacting with ethylene oxide. Another useful

25 modification of the acrylic ester latices is to incorporate up to as much as 20% of hydroxy alkyl esters of either acrylic or methacrylic acids.

Mixed Acrylic Ester Latices

As indicated it also within the scope of the invention to use physical mixtures of two or more acrylic ester latices for the purposes of the invention. Routine experimentation may be use to optimize such blends for purposes of the invention. Blends of acrylic ester latices are shown in U.S. Patent 2,795,564, which has previously been discussed.

Silicone Polymer Modification of the Acrylic Ester Latices

Improved results are achieved when the acrylic ester latices are modified to include silicone polymers. A variety of methods have been shown for combining silicones with acrylic esters. See U.S. Patent 5,202,368, the disclosure of which is incorporated herein by reference. A preferred method of combining the silicone resin with the acrylic ester latex is to use silicone emulsions which contain in emulsion form silicone polymers such as polydimethylsiloxane polymers. One such emulsion is sold by Dow Corning under the trade designation, Dow Corning Silicone Emulsion 365. While the amount of silicone resin on a dry weight bases may range between 0.001 to 3% by weight typically 0.1 to 2.5% will give good results. Amounts as great as 5% may be used but too much may produce adverse effects. These emulsions

may require modification to render them compatible and stable when they are blended with the acrylic ester latices.

Working Concentrations of the Acrylic Ester Latices:

5 Blending with the Coagulant Salts: Film Thickness

The acrylic ester latices are produced commercially in the form of concentrates which contain at least 20% and often in excess of 35% by weight of the acrylate ester polymer. It has been found that
10 these concentrated latices in many cases do not provide good quality mold or article coatings. In a preferred mode of the invention it has been found that good coatings are obtained when the latices are diluted with water to provide latices containing between 2-10% by
15 weight of the acrylate ester polymers. Concentrations of between 4-8%, most preferably 6%, give good results.

In order to provide an improved commercially workable process which provides good former release and at the same time simplify coagulation of the rubber
20 latex it is necessary that the diluted acrylic ester latex be fortified with at least 5-25% and preferably 10-20% by weight of a coagulating salt. These coagulating salts are most commonly inorganic salts of mineral acids such as the water soluble alkaline earth
25 salts of hydrochloric, sulfuric or nitric acids. Typically salts such as calcium chloride or calcium

nitrate provide satisfactory coagulation of most rubber latices. Salts of zinc and aluminum may also be used.

The salts when added to the acrylic ester latices in certain instances cause destabilization of the latex. To prevent this from taking place it is desirable that a stabilizing amount of a water soluble surfactant, preferably a non-ionic surfactant be added to the latex-salt mixture. This stabilization technique is described in the Kavalir patents previously cited. The amount and type of surfactant can only be determined by experimentation since the latex and particular coagulant salt will vary. Usually not more than a few percent of the stabilizer is necessary e.g. about from 0.1% to about 3% by weight. It will be understood that when the acrylic ester latices are used to form a coating on the inside of the finished article such as a glove it is not necessary nor desirable that the latex contain a coagulating salt. In a similar fashion it not necessary that the same latex used as the former mold release coating be used in the formation of the donning coating.

The thickness of the coatings applied to the former or to the formed article will vary and can be optimized by routine experimentation. The thickness of the former release coating need not necessarily be the same thickness as a donning coating. As a general rule the thickness of the coatings should not be not be

greater than 20% the thickness of the coating of the rubber latex article. Typically coatings as thin as 200 microns up to coatings of several mils may be used.

5

The Coating Process

Once the coagulation-inducing, powder-free composition is prepared, the former is dipped or immersed in the composition to form a film or first layer and is then withdrawn. After the former is withdrawn from the composition, the first layer is allowed to stand and dry or is dried in an oven at 70°C for about 3 minutes to form a coherent film or layer. Once dried, the first layer is capable of inducing conventional coagulation when dipped or immersed into a latex compound.

After the formation of the first layer, the former is then dipped into a latex compound to form a second layer. The latex compound can be any coagulatable natural or synthetic latex compounds, coagulatable natural or synthetic rubber latices or styrenic block copolymer dispersions known in the art. Conventional formulations for the preparation of latex are well known in the art and those skilled in the art are readily able to vary the formulations and conditions of curing and the like to suit the particular latex being used as well as the final article desired. Precured

or partially cured latex can be used; however, if non-cured latex is used, it must be cured after forming. Additionally, the latex may contain conventional compounding ingredients commonly utilized. Specific
5 examples are provided in U.S. Patent 3,411,982, hereby incorporated by reference.

When the former is immersed into the latex compound, the dried film induces coagulation of the latex to produce a uniform coagulated deposit of the
10 latex on the former. The length of time the former is immersed in the latex determines the wall thickness of the article. The longer the dwell time period, the greater the wall thickness of the article, and vice versa. Articles produced according to the method of
15 this invention typically have a thickness of between 4 to 15 mils.

The former is removed from the latex with a coating of gelled latex adhering to it. The former is placed in a water bath to leach out water soluble
20 components such as proteins, electrolytes, etc. The temperature of the water bath is between 49-60°C.

After leaching, the second layer maybe dried or coated with a lubricating polymer. If dried, then the first and second layers are cured. As used in this
25 invention, the term "curing" also includes "fusing" or "fusion" as some types of polymers require fusing instead of curing. For example, thermoplastic

elastomers such as the copolymers poly(styrene-b-isoprene-b-styrene) (SIS), poly(styrene-b-butadiene-b-styrene) (SBS), and poly(styrene-b-ethylene propylene-b-styrene) (SEPS) require fusing. Typically, however, curing is employed. The length of time required for curing depends upon the polymers selected, however, most polymers can be cured in about 5 to 10 minutes at about 138°C. After curing, the resulting article is allowed to cool and is removed from the former.

The acrylic ester latices when used as article coatings can be applied either before the drying of the second layer, after the drying of the second layer but before curing, or after curing. When applied, it will add additional layers to the already multi-layered article. After the acrylic ester latex is coated to the article, it is allowed to stand and dry or is dried in an oven. One skilled in the art would recognize that the conditions required for drying the lubricating polymer in an oven vary based on the type of lubricating polymer employed. If the acrylic ester polymer is added to the article prior to curing, the polymer may be dried and the article cured in one step.

If the polymer is applied after the article is cured, then it must be dried.

Stripping of the article from the former turns the article inside out so that the first layer is on the outside and the latex or lubricating layer is on the

inside. The stripping process does not require any powder to release the article from the former. Additionally, the resultant article is not tacky. The process of this invention results in multi-layered powder-free rubber articles. Examples of the types of articles that can be made pursuant to this invention include: surgical and examination gloves, catheters and condoms.

In the practice of the invention with respect to gloves, the molds used are in a variety of sizes and shapes corresponding to the various hand sizes for which the gloves are intended. The preferred mold is a contoured mold having a textured to highly polished ceramic or porcelain surface or one having a fluorocarbon coating, however, other molds such as glass, hard woods, and plastic can also be used. Gloves produced according to this method are easily removed from a former are not tacky, exhibit good donning characteristics, and are powder-free.

20

BENEFITS OF THE INVENTION

Articles produced according to this invention have many features and benefits. For example, articles made according to this invention can be made in a continuous fashion with significant economic savings as compared to the conventional processes used to make powder-free articles. The conventional processes used

to make powder-free articles are more expensive due to the number of chlorination, turning and drying steps involved in the manufacture.

5 A further advantage of this invention is that the process uses environmentally friendly materials. Unlike other processes used to make powder-free gloves, the process of this invention does not include a chlorination step. Chlorine is considered a toxic chemical and the use of a chlorination process to
10 remove powder from a rubber article raises numerous disposal and environmental issues. In addition, chlorinated products tend to discolor and age poorly both in storage and in use.

EXAMPLES

15 The following examples could be tried to demonstrate the process claimed in the aforementioned applicaiton. A coagulation inducing film could be deposited onto a former (ceramic or Halar) from an emulsion acrylic copolymer (e.g., Hycar 26256), diluted
20 with water to 6% by weight copolymer. This emulsion would be stabilized with a non-ionic surfactant so that the addition of calcium nitrate (20 wt%) does not destabilize the acrylic emulsion. The level of non-ionic surfactant could be selected in the preferred
25 range from 0.5 wt% to 6 wt.% , so that the emulsion does not destabilize during the addition of calcium

nitrate. The Hycar 25256 is manufactured by BF Goodrich and is understood to contain a copolymer of either acrylic or methacrylic acid of about 5% or more by weight with a lower alkyl acrylate ester (C₁ to C₄).
5 This material has a TG of + 45°C.

A silicone emulsion Dow Corning 365 could be added in an amount of approximately 1% by wt. to facilitate release from the mold.

The coagulation inducing film on the former after
10 drying could be dipped into the latex compound in a customary fashion to distribute the film uniformly around the former. The deposited coagulated film could be leached in warm water and a donning layer could be applied. It is expected a former treated with the
15 acrylate latex described above would show a 20% improvement in mold release. When combined with the silicone it is expected a 30% or more increase would be shown in mold release.

CONCLUSION

20 Although the invention has been described primarily in connection with the special and preferred embodiments, it will be understood that it is capable of modification without departing from the scope of the invention. The following claims are intended to cover
25 all variations, uses, or adaptations of the invention,

following, in general, the principles thereof and
including such departures from the present disclosure
as come within known or customary practice in the field
to which the invention pertains, or as are obvious to
5 persons skilled in the field.

I CLAIM:

1. A multiple dip process for making powder-free rubber articles comprising the steps of:

5 a) dipping a former of the desired shape of the article into a composition consisting essentially of an aqueous acrylic ester latex and water soluble salts capable of coagulating a rubber latex whereby a first layer lubricating coating is formed on the former;

10 b) dipping the former treated in step (a) into a rubber latex to produce a second layer;

c) leaching the second layer in water;

d) curing the first and second layers; and

e) stripping the resultant article from the former.

15 2. A multiple dip process for making powder-free rubber articles comprising the steps of:

a) dipping a former of the desired shape of the article into a composition consisting essentially of an aqueous acrylic ester latex whereby a first lubricating
20 coating is formed on the former;

b) dipping the former treated in step (a) into water soluble salts capable of coagulating a rubber latex;

25 c) dipping the former treated in step (b) into a rubber latex to produce a second layer;

d) leaching the second layer in water;
e) curing the first and second layers; and
f) stripping the resultant article from the former.

5

3. The multiple dip process of claims 1 or 2 which comprises the additional step of applying the composition which does not contain the water soluble salts to the second layer prior to curing.

10 4. The multiple dip process of claims 1 or 2 where which comprises the additional step of applying the composition which does not contain the water soluble salts to the article prior to stripping , but after curing, and then drying the composition.

15 5. The multiple dip process of claims 1 or 2 where the aqueous acrylic ester latex is an acrylic acid or methacrylic acid ester latex which contains from 4 to 22 carbon atoms.

20 6. The multiple dip process of claim 5 where the aqueous acrylic ester is a copolymer which contains from 2-3 monomers. .

7. The multiple dip process of claims 1 or 2 where the aqueous acrylic ester latex is a mixture of acrylic esters.

25 8. A multiple dip process for making powder-free rubber gloves comprising the steps of:

a) dipping a former of the desired shape of the

glove into a composition consisting essentially of an aqueous acrylic ester latex wherein the acrylic ester is an acrylic ester containing from 0.1-20 weight percent of either acrylic acid or methacrylic acid and water soluble salts capable of coagulating a rubber latex whereby a first layer lubricating coating is formed on the former;

b) dipping the former treated in step (a) into a rubber latex to produce a second layer;

c) leaching the second layer in water;

d) curing the first and second layers; and

e) stripping the resultant article from the former.

9. A multiple dip process for making powder-free rubber articles comprising the steps of:

a) dipping a former of the desired shape of the article into a composition consisting essentially of an aqueous acrylic ester latex wherein the acrylic ester is an acrylic ester containing from 0.1-20 weight percent of either acrylic acid or methacrylic acid whereby a first layer, lubricating coating is formed on the former;

b) dipping the former treated in step (a) into water soluble salts capable of coagulating a rubber latex;

c) dipping the former treated in step (b) into a rubber latex to produce a second layer;

d) leaching the second layer in water;

e) curing the first and second layers; and
f) stripping the resultant article from the former.

10. The multiple dip process of claims 8 or 9 which
5 comprises the additional step of applying the composition which does not contain the water soluble salts to the second layer prior to curing.

11. The multiple dip process of claims 8 or 9 where
10 which comprises the additional step of applying the composition which does not contain the water soluble salts to the article prior to stripping , but after curing, and then drying the composition.

12. The multiple dip process of claims 8 or 9 where
15 the aqueous acrylic ester latex is an acrylic acid or methacrylic acid ester latex which contains from 4 to 22 carbon atoms.

13. The multiple dip process of claim 12 where the
aqueous acrylic ester is a copolymer which contains from 2-3 monomers.

20 14. The multiple dip process of claims 8 or 9 where the aqueous acrylic ester latex is a mixture of acrylic esters.

15. A multiple dip process for making powder-free rubber gloves comprising the steps of:

25 a) dipping a former of the desired shape of the glove into a composition consisting essentially of an aqueous acrylic ester latex, water soluble salts .

capable of coagulating a rubber latex and from 0.001-3% by weight of a silicone resin whereby a first layer lubricating coating is formed on the former;

- b) dipping the former treated in step (a) into a rubber latex to produce a second layer;
- c) leaching the second layer in water;
- d) curing the first and second layers; and
- e) stripping the resultant article from the former.

16. A multiple dip process for making powder-free rubber gloves comprising the steps of:

- a) dipping a former of the desired shape of the glove into a composition consisting essentially of an aqueous acrylic ester latex and from 0.001-3% by weight of a silicone resin whereby a first layer lubricating coating is formed on the former;
- b) dipping the former treated in step (a) into a rubber latex to produce a second layer;
- c) leaching the second layer in water;
- d) curing the first and second layers; and
- e) stripping the resultant article from the former.

17. The multiple dip process of claims 15 or 16 which comprises the additional step of applying the composition which does not contain the water soluble salts to the second layer prior to curing.

18. The multiple dip process of claims 15 or 16

where which comprises the additional step of applying the composition which does not contain the water soluble salts to the article prior to stripping , but after curing, and then drying the composition.

5 19. The multiple dip process of claims 15 or 16 where the aqueous acrylic ester latex is an acrylic acid or methacrylic acid ester latex which contains from 4 to 22 carbon atoms and the silicone resin is in the form of an aqueous emulsion.

10 20. The multiple dip process of claim 19 where the aqueous acrylic ester is a copolymer which contains from 2-3 monomers.

15 21. The multiple dip process of claim 15 or 16 where the aqueous acrylic ester latex is a mixture of acrylic esters.

22. A former for making powder-free rubber articles which contains a coating of the composition described in claims 1 or 2.

20 23. A former for making a powder-free rubber gloves which contains a coating of the composition described in claims 8 or 9.

24. A former for making a powder-free rubber gloves which contains a coating of the composition described in claims 15 or 16.

25 25. A rubber glove having its inner surface coated with the composition described in claim 3.

26. A rubber glove having its inner surface coated

with the composition described in claim 10.

27. A rubber glove having its inner surface coated with the composition described in claim 17.

INTERNATIONAL SEARCH REPORT

Int. .onal Application No

PCT/US 96/01816

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 B29C41/00 B29C41/14 B29C41/22		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 6 B29C B29D B29H A61B A41D A61F C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 082 862 (ESEMPLARE ET AL.) 4 April 1978 see column 3, line 27 - column 6, line 40 ---	1-14, 22-26
X	US,A,3 411 982 (KAVALIR JOHN J ET AL) 19 November 1968 cited in the application see column 1, line 62 - column 2, line 40; figures ---	1-14, 22-26
X	GB,A,1 052 546 (UNITED STATES RUBBER COMPANY) 21 December 1966 ---	2-7, 9-14, 22-26
Y	see the whole document ---	15-21,27
Y	EP,A,0 543 657 (JOHNSON & JOHNSON MEDICAL) 26 May 1993 see the whole document ---	15-21,27
-/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family		
Date of the actual completion of the international search 20 June 1996		Date of mailing of the international search report 4. 07. 96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016		Authorized officer Mathey, X

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/01816

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 027 060 (EEMPLARE PASCAL E ET AL) 31 May 1977 see column 3, line 5 - column 6, line 40 ---	1-14, 22-26
X A	WO,A,84 00908 (LRC PRODUCTS) 15 March 1984 see the whole document ---	22-24 5-7, 12-14, 19-21
X A	GB,A,806 142 (INTERNATIONAL LATEX CORPORATION) 17 December 1958 see the whole document ---	22-27 1-21
A	CA,A,2 128 670 (SMITH & NEPHEW INC.) 6 February 1995 see the whole document -----	1,2,8,9, 15,16, 22-27

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/01816

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4082862	04-04-78	US-A- 4027060 AU-B- 8529675 CA-A- 1049345 CH-A- 610814 DE-A- 2628059 FR-A- 2315382 GB-A- 1492330 JP-C- 995308 JP-A- 52004581 JP-B- 54032665	31-05-77 03-03-77 27-02-79 15-05-79 27-01-77 21-01-77 16-11-77 30-04-80 13-01-77 16-10-79
US-A-3411982	19-11-68	BE-A- 661287 FR-A- 1434453 NL-A- 6503238 US-A- 3286011	16-07-65 20-06-66 20-09-65 15-11-66
GB-A-1052546		NONE	
EP-A-0543657	26-05-93	US-A- 5284607 AT-T- 133054 AU-B- 654407 AU-B- 2831792 BR-A- 9204500 CA-A- 2083480 DE-D- 69207730 ES-T- 2083108 FI-A- 925287 JP-A- 6022981	08-02-94 15-02-96 03-11-94 27-05-93 15-06-93 23-05-93 29-02-96 01-04-96 23-05-93 01-02-94
US-A-4027060	31-05-77	US-A- 3919442 AU-B- 8529675 CA-A- 1049345 CH-A- 610814 DE-A- 2628059 FR-A- 2315382 GB-A- 1492330 JP-C- 995308 JP-A- 52004581 JP-B- 54032665 US-A- 4082862	11-11-75 03-03-77 27-02-79 15-05-79 27-01-77 21-01-77 16-11-77 30-04-80 13-01-77 16-10-79 04-04-78

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/01816

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4027060		AU-B- 7399374 CA-A- 1030411 CH-A- 605103 DE-A- 2448326 FR-A,B 2247340 GB-A- 1452366 JP-C- 944535 JP-A- 50078681 JP-B- 53022118 US-A- 3967014	08-04-76 02-05-78 29-09-78 17-04-75 09-05-75 13-10-76 20-03-79 26-06-75 06-07-78 29-06-76
WO-A-8400908	15-03-84	AU-B- 570646 AU-B- 1949483 AU-B- 598061 AU-B- 8126887 CA-A- 1225508 DE-A- 3378527 DE-A- 3382663 DE-A- 3382677 DK-B- 170783 EP-A,B 0105613 EP-A,B 0198514 EP-A,B 0199318 JP-A- 5001161 JP-B- 7017771 US-A- 4499154 US-A- 4575476 US-A- 4548844	24-03-88 29-03-84 14-06-90 10-03-88 18-08-87 29-12-88 08-04-93 27-05-93 15-01-96 18-04-84 22-10-86 29-10-86 08-01-93 01-03-95 12-02-85 11-03-86 22-10-85
GB-A-806142		NONE	
CA-A-2128670	06-02-95	AU-B- 6871594 EP-A- 0640623 JP-A- 7062003 ZA-A- 9405853	16-02-95 01-03-95 07-03-95 05-04-95